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Light Scattering Studies in Aerosols with a New Counter-Photometer

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ABSTRACT

A versatile light scattering instrument of high sensitivity is described. It employs a right-angle collecting system. It can be used (a) to determine the distribution of particle sizes in aerosols, by counting and classifying individual particles, and (b) to record the light scattering intensities from aerosols and gases.

Procedures have been developed for calibration of the counter with the uniform polyvinyltoluene and polystyrene latex preparations. The degree of monodispersity of a test aerosol produced by spray-drying these preparations was considered in detail. Pulse amplitude distribution measurements were made on 0.33, 0.5, and 1μ diameter particles. The results indicate that the scattering signal per particle, in our optical system, is proportional to the square of the diameter. The resolving power of the counter lies within a standard deviation of 8 percent in particle diameter.

Methods were developed to employ gases as standards for particle counting work. It was found that the measured scattering intensities from He, H₂, N₂, CO₂, SO₂, and CH₃Cl increase with the square of the mean molecular polarizabilities, as expected. The limit of sensitivity of the photometer corresponds to 7.3×10^{-11} g./liter of a 0.3μ diameter test aerosol.

Introduction

Light-scattering measurements on aerosols have been used intensively since 1942, and are well established for the determination of relative concentrations¹ under conditions such that the particle-size distribution

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- (1) F. T. Gucker, Jr., H. B. Pickard, and C. T. O'Konski, "Handbook of Aerosols," Atomic Energy Commission, Washington D.C., 1950, Ch. 10.
-

of the aerosol remains unchanged. Sensitive instruments, such as the one developed at Northwestern University in 1943, and described later,² were

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- (2) F. T. Gucker, Jr., H. B. Pickard, and C. T. O'Konski, J. Am. Chem. Soc. 69, 429 (1947).
-

capable of detecting 10^{-9} g./l., or around 70 particles/cc., of an oil smoke consisting of droplets around 0.3 micron (μ) diameter. For particles above 0.6μ diameter, much greater sensitivity was achieved with the development of the first instrument capable of electronically counting the aerosol particles^{3,4} individually. Subsequent refinements of this instrument⁵ were

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- (3) F. T. Gucker, Jr., C. T. O'Konski, H. B. Pickard, and J. N. Pitts, Jr., J. Am. Chem. Soc. 69, 2422 (1947).

- (4) F. T. Gucker, Jr., and C. T. O'Konski, Chem. Reviews 44, 373 (1949).

- (5) F. T. Gucker, Jr., and C. T. O'Konski, J. of Colloid Science 4, 541 (1949).
-

directed toward the determination of size distribution in aerosol systems.

At the extremely low concentrations necessary for counting of particles separately, experimental difficulties encountered in producing and maintaining aerosols of very uniform and accurately known particle size precluded adequate testing of the refined model⁵ of the instrument.

Recently, there have been produced⁶ uniform spherical particles of

(6) Physical Research Laboratory, The Dow Chemical Company, Midland,
Michigan.

polystyrene (PS) and polyvinyltoluene (PVT) in the size range from 0.1 to 1 μ . Such particles, when dispersed individually as an aerosol, are ideal for calibration and evaluation of counting instruments because of their high degree of uniformity and their low vapor pressures. We are presenting the results of experiments on several of the uniform preparations, which establish that the light-scattering particle counter is feasible for the rapid determination of size distribution in aerosol systems.

The present instrument is both a refinement and a combination of previous photometers and counters. With it, we have been able to continuously record the average light scattering intensities from very dilute aerosols, and simultaneously conduct counting experiments on the same system. Relative scattering intensities for some of the latex particles have been determined. In addition, the relative light scattering intensities from various gases have been measured, and procedures have been devised for the use of gases as standards for this work.

A number of factors which enter into the interpretation of the results are discussed, and the performance of the instrument is evaluated.

The Light Scattering Instrument

A schematic diagram of the apparatus is shown in Fig. 1. The principles of operation are as follows: Aerosol particles in a suitably defined stream, perpendicular to the plane of the diagram, are passed through the region designated by the dark spot at the intersection of the dashed lines. This region is intensely illuminated by means of the light source S, in conjunction with the lenses L₁ and L₂, the aperture S₁, and the field stop S₂. Particles entering it scatter a small fraction of the incident light. The scattered light within a large solid angle in the vicinity of 90° is collected by the lenses L₃, and brought to focus in the plane of the field stop S₉, from which it proceeds to the cathode of a photomultiplier tube, P. Since the particles traverse the illuminated region in a period of the order of a millisecond, the electrical signals at the photomultiplier appear in the form of pulses, with amplitudes which depend upon the flux reaching the photocathode. The pulses are sent to discriminator and counter circuits for pulse amplitude distribution analysis, as discussed below, and the D.C. component of the photomultiplier current is presented on a recorder.

The optical system was chosen after considerable experimentation with various arrangements. Both small-angle and right-angle light collecting systems were set up. Various glare stops and especially designed knife-edged light traps were tested. The right-angle system proved to have a greater sensitivity for sub-micron particles than the small-angle arrangement which we tested, and it was adopted for this work. In its final form, there were several modifications from the earlier instrument,⁵ which include

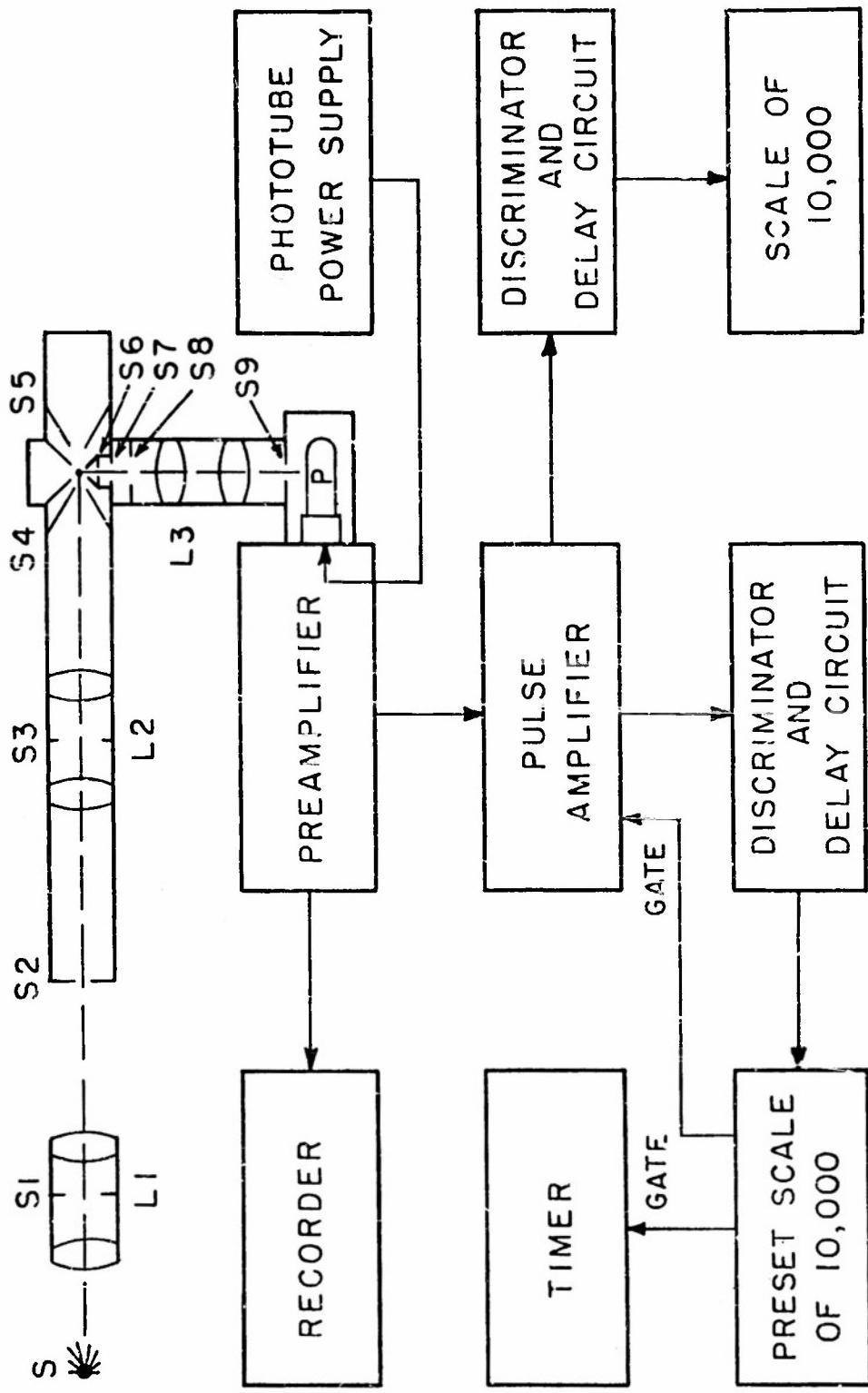


FIG. I SCHEMATIC DIAGRAM OF THE LIGHT-SCATTERING COUNTER- PHOTOMETER

(a), insertion of various additional stops, S3 to S8, and (b), reduction of the dimensions of the slits and the diameters of the aerosol and shcath-air tubes. By these means, the background flux to the photomultiplier detector was reduced, which resulted in a decrease of the random noise, and an increase of the sensitivity and precision for weak signals.

The field stops S2 and S9 were rectangular 0.10×0.20 cm. slits. The longer dimensions were transverse to the aerosol tube axis. The internal diameter of the aerosol tube was 0.15 cm. The total scattering volume, v_t , was 0.004 cc., and the sensitive volume, v_s , was 0.0017 cc.*

* We define the total scattering volume as that volume which is both illuminated by the source and viewed by the photomultiplier. For comparison of various right-angle optical systems, it can be calculated as the product of the slit (S2) dimension, measured transversely to the direction of the aerosol tube axis, the slit (S9) dimension, similarly transverse, and the smaller of the two remaining dimensions of S2 and S9. This assumes rectangular slits and neglects the effect of the slight spreading at the focal region due to convergence.

The sensitive volume is defined as the volume of the aerosol stream both illuminated and viewed. Since the transverse dimensions of S2 and S9 completely cover the stream, so that all particles are counted, it can be calculated as the product of the area of the aerosol stream at the focal region, and the third dimension employed in the total scattering volume calculation.

With the previous right-angle optical system⁵, v_t and v_s were about 0.016 and 0.008 cc., respectively. This situation was not properly evaluated in reference 5.

The photoelectric detector, P, was the better of two RCA 1P21 photomultipliers which we tested. Both tubes had somewhat higher signal-to-noise ratios in this application than any of the earlier 931 and 931-A tubes⁵, some of which were retested in this research. This is undoubtedly the result of improved manufacturing procedures. The regulated high-voltage power supply was a circuit of the Higinbotham type⁷. The photomultiplier

(7) W. A. Higinbotham, Rev. Sci. Insts. 22, 429-431 (1951).

dynode voltages were obtained from a resistance divider network. The output impedance was 10^7 ohms shunted by the distributed capacity, about 20 $\mu\mu$ fd., which decreased the noise level by suppressing high-frequency response. The photomultiplier was direct-coupled to a differential cathode-follower amplifier⁸.

(8) Elmore and Sands, "Electronics", McGraw-Hill Book Co., Inc., New York, 1949.

The D.C. signal was filtered and applied through a variable attenuating circuit to a 2.5 millivolt (mv.) Brown potentiometer-type recorder. Suitable zero-balance and measuring circuits were incorporated into the D.C. network, which was used for the photometric measurements, and precautions were taken to ensure high stability. The output current of the photomultiplier was at times measured potentiometrically by means of a helipot provided for the purpose.

The A.C. signal from the differential amplifier was increased about 100-fold in the capacitively coupled feedback amplifier, which employed

compensated networks to ensure faithful reproduction of pulses. The amplifier output stage was a gated cathode follower. The gate signal was derived from a preset scaler, and turned off the output stage after a predetermined number of counts. The differential amplifier was so arranged that signals were clipped at about two volts, to prevent blocking of the amplifier and the discriminator circuits on relatively large pulses.

The amplified signals were fed to electronic discriminators of the Schmitt type⁸. Each discriminator provided a rectangular output pulse whenever the signal exceeded a bias level, which was accurately and conveniently adjusted between zero and 100 volts by means of a helipot. The discriminators were capacitively coupled to the cathode follower output stage of the amplifier, and clamping circuits were inserted at the grids to ensure rapid recovery after large pulses, and to maintain the proper reference level at higher counting rates.

The output from each discriminator was passed through a differentiating circuit and into a univibrator. This unit was so arranged that upon being triggered, it was not affected by a second pulse occurring within an interval T_d of the one preceding. The delay time, T_d , was made slightly longer than T_a , the duration of the pulse from an aerosol particle. This provided an electrical delay which insured that pulses in coincidence would always be recorded as one pulse, and that multiple counting of individual pulses could not occur. It can readily be shown that, because of the random noise, pulses with amplitudes near the discriminator bias level would at times be counted more than once, unless some sort of electrical delay were incorporated. This was verified by experiment, as discussed below.

The large output pulses from the univibrators, or delay circuits, were differentiated and fed to corresponding scalers, which consisted of decade units of the modified binary type⁹. For this research, two discriminators

-
- (9) Berkeley Scientific Division, Beckman Instruments Company, Richmond, California. The simple decades were type 700A, and the preset decades, type 730. These units have a resolving time of 5 microseconds.
-

and two scales of 10,000 were assembled. One of the scaling circuits contained two preset decades so that after beginning an experiment, counting would proceed through the interval corresponding to any preset integral number, between 1 and 99, of hundreds of counts on this scaler. After this interval a gate signal was automatically applied to the amplifier, which stopped all counting, and to a relay circuit, which controlled a timer. Appropriate circuitry was incorporated to reset the scalers and timer electrically. All power supplies were electronically regulated wherever the voltages affected the operation of the discriminators, and quality components were employed for the critical circuit elements. In the differential preamplifier circuit, where plate and cathode circuit current was low, and extreme stability was desired, two small batteries were employed. Details of the circuitry, together with scale drawings of the optics, will be published later.

Experimental Procedures

Production of Aerosols - Aerosols were generated from hydrosols by the spray-dry technique which has been employed in previous work.^{3,5,10}

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- (10) R. M. Ferry, L. E. Farr, Jr., and M. G. Hartman, Chem. Reviews 44, 389 (1949).
-

A Vaponephrin⁴ nebulizer was employed with a primary air pressure of 5 lbs./in.², and 30 liters per minute (l/min.) diluting air. The primary air stream was humidified to reduce evaporation losses and resulting concentration changes in the hydrosol. The diluting air stream was pre-dried in a CaCl₂ tower. Both air streams were filtered with multiple pads of asbestos-filled paper.

The Latex Preparations - Experimental samples of polyvinyltoluene and polystyrene latex hydrosols were supplied by the Dow Chemical Company⁶. The six samples we received had particle diameters from 0.132 to 0.986 μ , with standard deviations, determined from electron micrographs, of 1 to 7 percent. Table 1 gives the Dow run number, the composition, the mean diameter, the standard deviation, and the number of particles from which the statistical data were obtained by the Dow laboratories.

Table 1. Uniformity of the Latex Particles⁶

<u>Run No.</u>	<u>Composition*</u>	<u>Mean Diameter</u> <u>Microns</u>	<u>Standard Deviation</u> <u>Per Cent</u>	<u>Number of Particles</u>
44-D	PVT	0.986	1.6	21
15N-8	PS	0.514	2.1	209
44-A	PVT	0.470	1.1	29
15N-7	PS	0.333	2.1	285
40	PVT	0.144	2.8	76
15N-23	PS	0.132	6.8	447

* PVT = polyvinyltoluene; PS = polystyrene.

The preparations as received contained around 30 percent solids by weight, and a small amount of stabilizer of unspecified composition. For aerosol generation, each sample was diluted to a particulate concentration of about 10^8 /cc., to reduce the aerosol concentration to an appropriate level, and to improve uniformity. (See Discussion.)

Light Sources - The sources in this work were the ribbon-filament tungsten lamp, and the 100 watt concentrated arc discussed previously⁵. The tungsten source was employed with an image-to-object ratio of unity, but the concentrated arc was used with a linear ratio of about two, in order to cover the field stop, S2, adequately. Operation was at the

manufacturer's rated values, 6 volts at 18 amperes for the ribbon-filament lamp, and 115 volts applied through a ballast resistor of 15.5 ohms to provide 6.25 amperes for the concentrated arc lamp.

Sampling Arrangement; Optics - The aerosol sample was taken from the open end of the spray-dry generator through a short length of tygon tubing to the central aerosol tube. The flow rate was set at 100 cc./min. by maintaining this difference between the exhaust and sheath-air flow rates, following the procedure discussed in earlier work.^{3,5} Since the test aerosols used here were relatively uniform and in the submicron region, fractionation was not a problem, and no special precautions were required in setting up the sampling arrangement.

The field stop dimensions are given above. The half-angle of the scattered light collecting lens system was 15.6°. That of the illumination system, determined by the aperture S1 of Fig. 1, was 12.2° with the tungsten source, and 10.8° with the concentrated arc source.

The pulse length estimated for these conditions, assuming uniform flow of the aerosol through the cross section of the stream, was 1.06 milliseconds (msec.); that experimentally observed with a triggered oscilloscope was 1.0 msec.

Photometric Measurements - Because the sensitive volume, defined in the footnote on page 6, normally depends upon the flow rates, the measurements on gases were made after flushing the entire cell with the carefully filtered gases. This results in improved precision, because the total scattering volume is then a function of the optical dimensions only.

An alternative procedure would be to arrange the aerosol stream diameter and the stop dimensions in such a manner that, allowing for extreme variations in the flow rates, the sensitive volume would always be filled completely with the stream being measured. This would make the sensitivity independent of flow rates. In addition, it would utilize the sheath-air system to prevent mixing of the aerosol with the contents of the cell, and flushing time could be reduced to a fraction of a second.

After adjusting the photomultiplier voltage and the attenuating circuit to appropriate levels, generally ascertained by means of a preliminary experiment, the deflections of the recorder were observed, first with the illumination on, and then cut off by a shutter. The difference in deflections was a measure of the photocurrent, excluding dark current. By operating the recorder during the flushing operations, it was conveniently observed when the deflection reached a steady value, which required about two minutes.

The relative gain of the photomultiplier was measured for voltages from 41.6 to 125 per stage. The gain curve was slightly steeper than that for an average 1P21¹¹. At our relative gain of 1.00 (55.5 volts per stage)

(11) RCA Tube Handbook 3, Vols 1-2, Tube Dept., Radio Corporation of America, Harrison, N. J., sheet 92CL-6454R2 (Oct. 26, 1949).

the average 1P21 has a current amplification of 3.5×10^4 .¹¹

Counting Procedures - Because coincidences contribute relatively large pulses, even when the aerosol particles are uniform, it is desirable to

reduce the fraction of coincidences to a negligible value. The number of coincidences of two particles within the sensitive volume, v_s , can be reduced to a small fraction of the number of particles if one adjusts the aerosol particulate concentration, n_a , to a value such that $n_a v_s \ll 1$. Treating the occurrence of a second particle within the sensitive volume as a random event, the fraction of coincidences is then simply $n_a v_s$. An alternative and equivalent expression of the fraction of coincidences, when the pulses are all of equal length, is $T_p r$, where T_p is the duration of a pulse, 0.001 second, and r is the count rate per second. Accordingly, the concentration was adjusted in each experiment until $T_p r$ equalled the desired coincidence level. In the experiments reported below, this was always less than 2 percent.

The photomultiplier gain was generally adjusted to a level such that the mean pulse amplitude was between 10 and 50 volts at the discriminators. For detection of signals which were just above the noise, it was desirable to have the noise level 10 to 100 times the limit of precision of the discriminator circuits, which was found to be 0.1 volt. When necessary, the background count rates due to random noise were subtracted from the observed rates at each discriminator setting, and corrections for the dead time in the circuit were applied.

Working Definition of Noise Level - In previous work⁵, the amplification in the electronic system was adjusted until the average noise level reached an arbitrary predetermined value. For computation of signal-to-noise ratios in this work, we have defined the noise level as that setting of the discriminator at which the random noise fluctuations, produced by the

steady background flux with air in the cell, resulted in 300 counts per minute (c./min.). This definition, which is by necessity arbitrary, was convenient because the noise level could be accurately measured with the counting equipment.

Experimental Results

Oscillographic Experiments - The first tests of the instrument were made before the stops S4 to S8 were incorporated into the optical system. A knife-edged light trap was placed in the region occupied by S5, and a stop was inserted conjugate to it, between S2 and L2. The negative output pulses from the preamplifier were applied directly to the input of a calibrated Tektronix 513-D oscilloscope. For these studies the aerosol flow rate happened to be 50 cc./min., which was one-half the usual value. Oscillograms were obtained on Linograph Pan film with a 35 mm. flash camera. By means of a simple circuit involving the flash contacts on the camera, the oscilloscope was triggered once each time the shutter was opened. Sweep rates were 5 or 10 msec./cm. The 0.98μ PVT hydrosol was diluted a factor of 10^3 , giving around 10^9 particles/cc. Fourteen exposures, totalling 1.00 sec., were made. A total of fifty-one pulses was observed. The duration and amplitude of each pulse was measured* by a procedure chosen

* We are happy to acknowledge the assistance of Mr. Jon Applequist in compiling data from the oscillograms.

to average out the noise and baseline variations. The average pulse duration was 2.0 msec. Certain of the pulses were rejected. These included one only partially visible on the oscillogram, five which were 2.6 msec. or

longer, evidently coincidences, and one with a peculiar shape which suggested a coincidence. By this procedure only imperfect coincidences were rejected while the exact ones would not be detected. Since any consideration of amplitudes in rejecting pulses would be liable to subjective errors, only duration and shape were accepted as criteria for rejection. The resulting number distribution in 10 millivolt intervals is illustrated in Fig. 2. One of the pulses, evidently an aggregate or dust particle, appeared with an amplitude of 387 mv., which is off the diagram.

A similar analysis was made of the pulse amplitude distribution obtained from the 0.470μ diameter PVT latex, spray dried after dilution by a factor of 10^4 . Forty pulses were recorded on five oscilloscopes, covering 0.50 sec. Only one pulse of 3.1 msec. duration was significantly longer than 2.0 msec., and it was rejected accordingly. The resulting pulse amplitude distribution in 5 mv. intervals is presented in Fig. 3.

Examples of the oscilloscopes are given in Fig. 4. Pulses were clearly well above the noise amplitude, which can be estimated from the traces by referring to the caption.

Photometric measurements were made during these experiments. The relative gain of the photomultiplier was 2.00, referred to our arbitrary figure of 1.00 at 55.5 volts per stage. The calculated anode photocurrents, normalized to a relative gain of unity, are summarized in Table 2, which also contains values for the relative scattering intensities per particle.

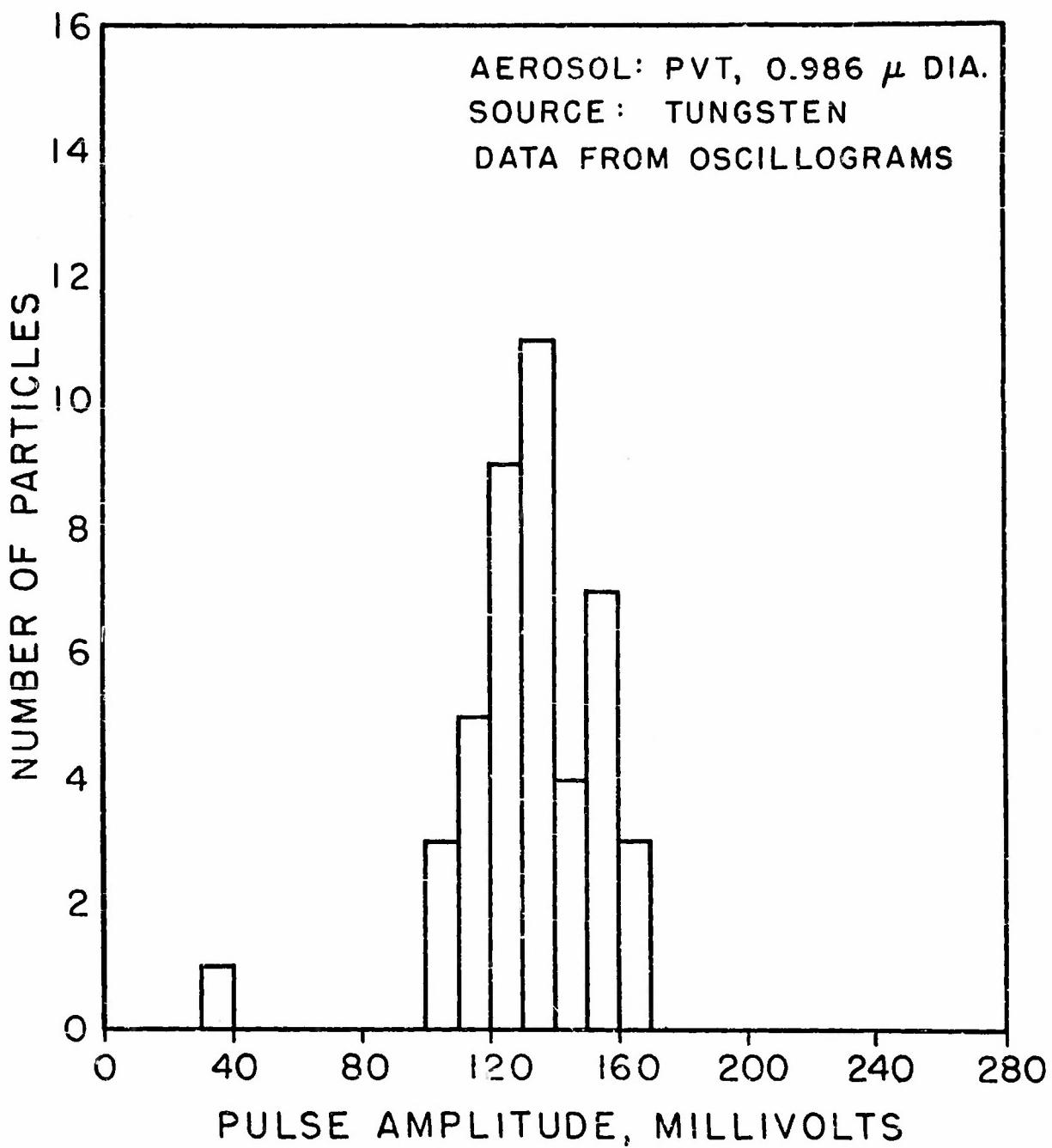


FIG. 2 PULSE AMPLITUDE DISTRIBUTION

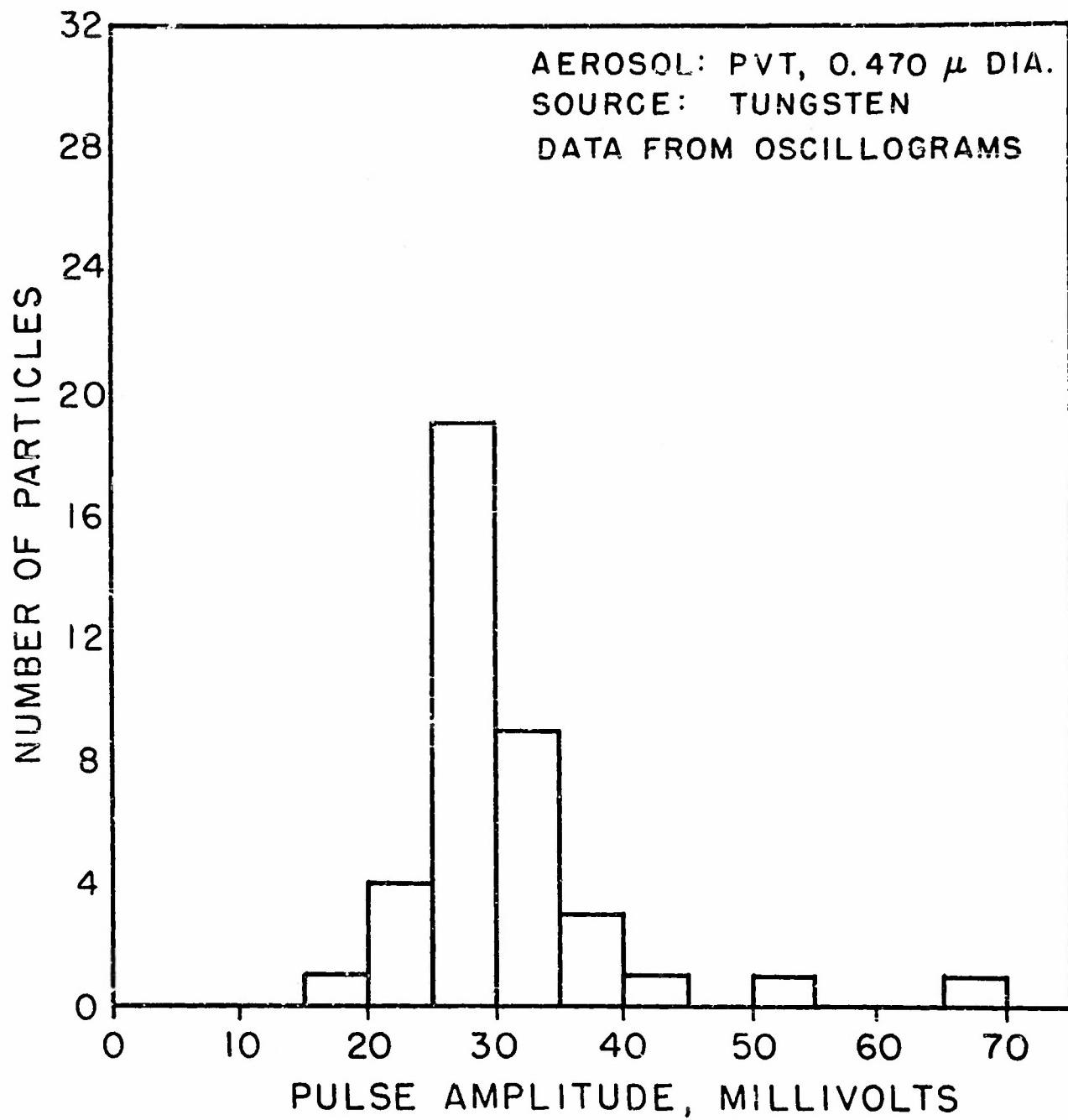


FIG. 3 PULSE AMPLITUDE DISTRIBUTION

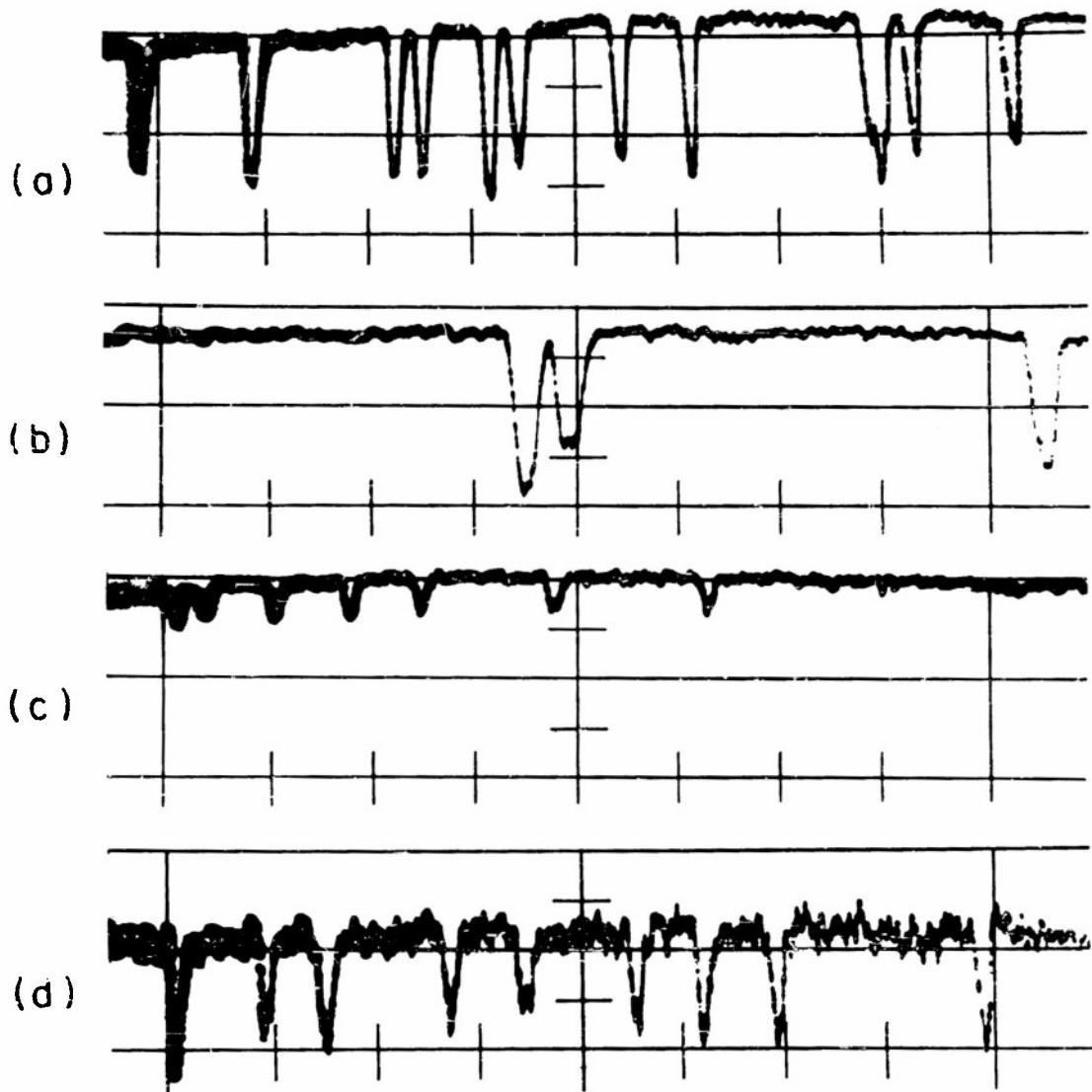


Fig. 4. Oscillograms of Pulses from the PVT Particles.

(Time is along the horizontal axis, 1 div. = 1 cm.)

0.986μ : (a) 10 msec./cm.; 100 mv./cm.

(b) 5 msec./cm.; 100 mv./cm.

0.470μ : (c) 10 msec./cm.; 100 mv./cm.

(d) 10 msec./cm.; 30 mv./cm.

Table 2. Summary of Results from
Oscillograms and Photometric Measurements

Scattering From:	Normalized Mean Pulse (amps. $\times 10^9$)	Normalized D.C. (amps. $\times 10^9$)	Normalized Particulate Concentration cc. $^{-1}$	Relative Signal From Mean Pulse	Relative Signal From D.C. Current
0.986 μ PVT	6.7*	0.72	71	1.00	1.00
0.470 μ PVT	1.5	0.23	96	0.23	0.24
Air†	--	0.52	--	--	--
Stray Light	--	0.69	--	--	--

* The two extreme pulses observed in this experiment were excluded, in order to obtain the best average for the main group of particles.

† Filling total scattering volume.

Electronic Counting Experiments - Count rate data were plotted against discriminator bias and a smooth integral counting curve was drawn. An example of results obtained with a single counting channel, and not corrected for the small background count, is illustrated by Fig. 5. Smoothed values of the count rates were read from the integral curves at constant bias intervals. The differences between successive rates are the count rate frequencies within the interval, and were taken as those corresponding to the mid-points of the intervals. The resulting frequency distribution, which is shown graphically in Fig. 6 for the data of Fig. 5, was treated by the usual statistical procedures¹² to obtain the mean pulse height and the

(12) See, e.g., Paul G. Hoel "Introduction to Mathematical Statistics", John Wiley and Sons, Inc., New York, 1947, Chapter II.

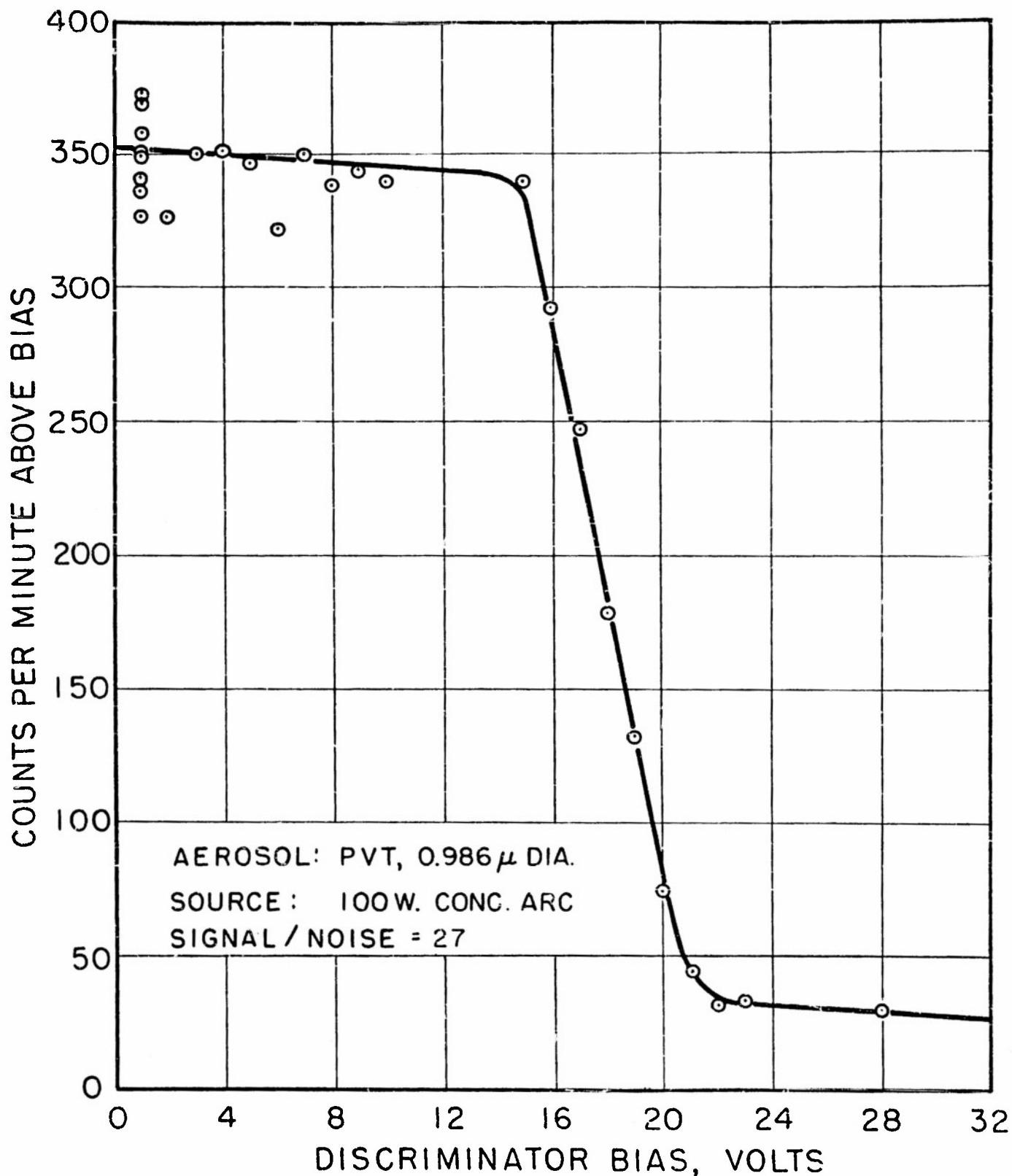


FIG. 5 INTEGRAL COUNTING CURVE
(EXPERIMENT 12-Zr-PVT)

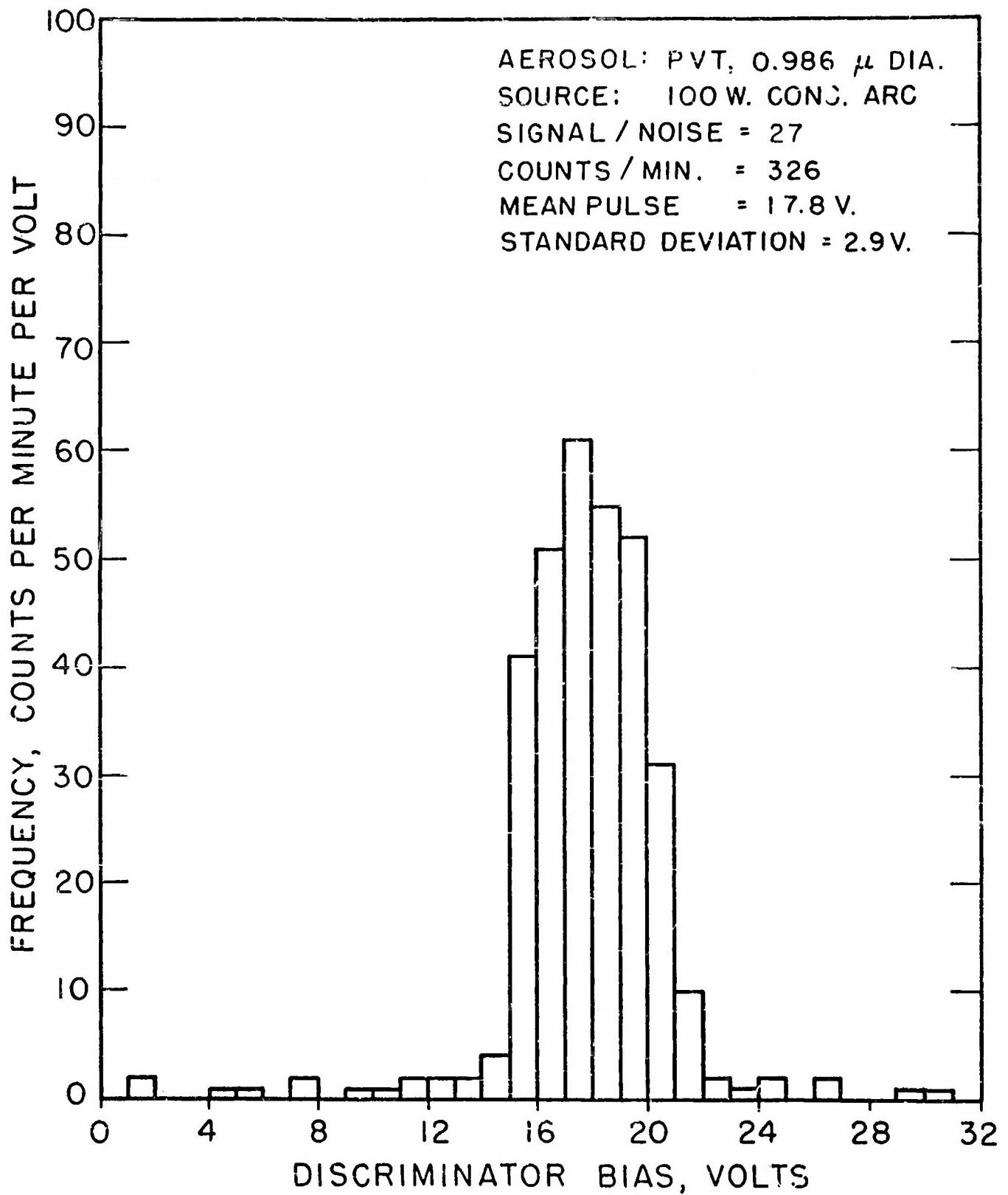


FIG. 6 PULSE AMPLITUDE DISTRIBUTION
(FROM FIG. 5)

standard deviation from the mean. The correction of the standard deviation for the effect of artificially grouping a continuous distribution into a discrete distribution¹³ turned out to be negligible, with our choice of

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- (13) Harold Cramér, "Mathematical Methods of Statistics", Princeton University Press, Princeton, 1951, pp. 359-363.
-

intervals, compared to the probable error in the standard deviation.

The procedure was applied to count rate data for several latex preparations. Results are presented in Table 3.

Table 3. Results of Electronic Counting Experiments

Experiment	Mean Diameter Microns	Mean Pulse, Volts	Standard Deviation, Per Cent	Signal Noise	D.C. Photocurrents Normalized		
					Stray Light, amps. $\times 10^9$	Air Scattering, amps. $\times 10^9$	Pulse Current, amps. $\times 10^9$
11-W-PVT	0.986	5.8	28	8.4	1.35	0.69	7.9
12-Zr-PVT	0.986	17.8	16	27	9.3	5.3	8.4
53-Zr-PS	0.514	26.5	14	7.3	1.1	2.54	2.36
54-Zr-PS	0.333	12.1	11	3.3	1.1	2.54	1.09

The experiment number, light source, and aerosol material are indicated by a composite experiment number in column 1. W indicates the tungsten ribbon filament source, Zr the Western Union concentrated zirconium arc. The observed mean pulse voltage and the standard deviation for each experiment are given in columns 3 and 4. The ratios of mean pulse height to the 300 c./min. noise level for each aerosol are given in column 5. Columns 6 and 7 contain the values of the photocurrent, at our relative gain of 1.00,

arising from stray light and scattering by air in the total scattering volume. The mean pulse voltages of column 3 were converted to photocurrent at the photomultiplier anode by dividing by the product of the anode resistance, 10^7 ohms, and the voltage gain from anode to discriminator. The resulting values were then normalized to a relative gain of unity, and a standard source intensity, to give the normalized pulse currents of column 8. The standard source chosen was the tungsten lamp employed in Exp. 11-W-PVT. Relative source intensity was determined from measurements of the intensities of light scattering from the air (alone) in each experiment, which appear in column 7. Thus, air serves as the calibrating medium for the instrument. Experiments 11 and 12 were carried out before the stops S6 to S8 were inserted, and with a single channel counter, with no electrical delay. The light source was replaced between experiments 12 and 53.

Typical integral count rate curves for counts due to noise at several photomultiplier gains are shown in Fig. 7. The concentrated arc source was used during these experiments and the background light levels were those prevailing during experiment 12. No electrical delay was used in determining these rates. Non-linear scales are used in Fig. 7 in order to obtain approximately straight lines to facilitate extrapolation. The ordinate is logarithmic and the abscissa is linear in the square of the bias voltage. An additional experiment was conducted on the 0.514μ PS to determine the magnitude of the error introduced by double counting. One channel with and another without the delay circuit were employed. Count rates at equal discriminator settings were found to be the same on the flat portions of the count rate curve. In the region of the mean pulse voltage, the circuit

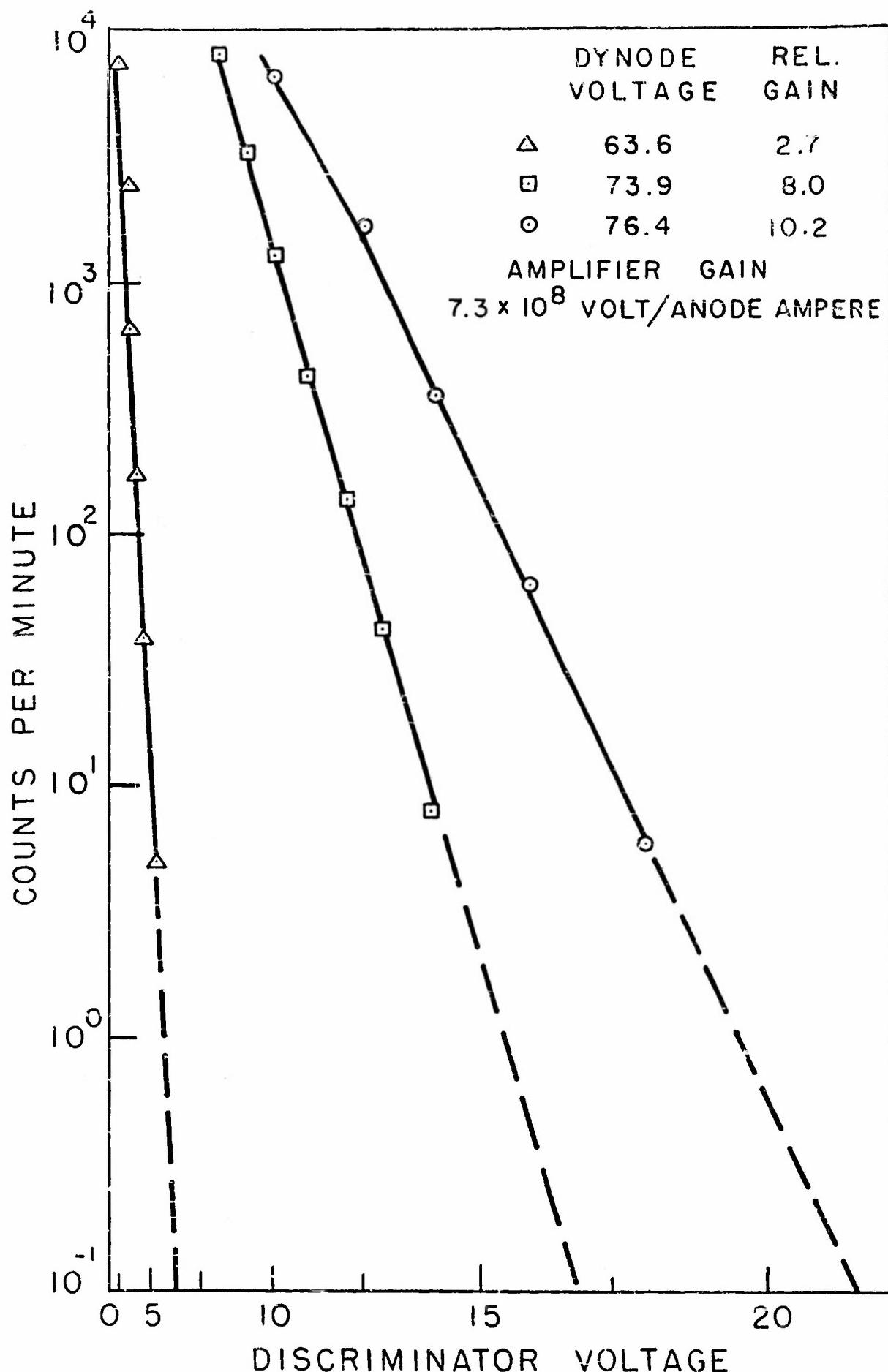


FIG. 7 COUNTING RATE PRODUCED BY NOISE

without delay gave count rates around 10 percent higher than the other, which were attributed to multiple counting of single pulses.

Photometric Measurements on Gases - The results of measurements of the light scattering intensities from various gases at 25°C. and 752 mm. pressure are shown in Table 4.

Table 4. Photometric Measurements on Gases*

Gas	Total Photocurrent (amps. $\times 10^9$)	Gas Scattering Photocurrent (amps. $\times 10^9$)	Molecular Polarizability esu, cc. $\times 10^{25}$	Calculated Molecular Polarizability esu, cc. $\times 10^{25}$
He	4.35	0.15	2.13	--
H ₂	6.47	2.27	7.8	8.3
N ₂	14.7	10.5	17.6	17.8
Air	14.9	10.7	--	--
CO ₂	28.8	24.6	26.6	26.2
SO ₂	58.9	54.7	40.6	--
CH ₃ Cl	76.5	72.3	46.3	46.7

* Experiment Index No. 50.

The gases, obtained from cylinders, were filtered and run continuously through the cell, following the procedure given in Photometric Measurements above. The relative photomultiplier gain for these experiments was 14.6. Column 2 of Table 4 gives the total photocurrent, uncorrected for background light. Column 4 lists molecular polarizabilities, which were calculated by means of the Lorentz equation¹⁴ from the refractive indices of the gases

(14) C. J. F. Bottcher, "Theory of Electric Polarisation", Elsevier Pub. Co., New York, 1952.

for the sodium D lines¹⁵, with the exception of CH_3Cl , which was calculated

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- (15) "Handbook of Physics and Chemistry", Chemical Rubber Publishing Co., Cleveland, Ohio, 29th edition, 1945, page 2188.
-

from the molar refraction obtained from atomic refractions¹⁶. The total

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- (16) F. Eisenlohr, Z. Phys. Chem., 75, 585 (1910); see also "Physical Methods of Organic Chemistry", A. Weissberger (Ed.) Interscience Pub., Inc., New York, 1949, Ch. XX, by N. Bauer and K. Fajans.
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photocurrent, i , was expressed as the sum of two parts, i_{sl} , due to stray light, which was considered constant, and i_g , due to scattering from the gas, which is proportional to the square of the molecular polarizability¹⁷.

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- (17) H. A. Stuart, "Molekulstruktur", J. Springer, Berlin, 1934.
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Thus

$$i = i_{sl} + i_g = i_{sl} + ka_g^2, \quad (1)$$

where k is proportional to the number of molecules per cc., and is a complicated function of the intensity and spectral distribution of the source, various parameters of the optical system, the sensitivity and spectral response of the photocathode, and the gain in the photomultiplier. A correction for the depolarization of the scattered light, which would be small, was not applied. From the data on helium and SO_2 , i_{sl} and k were evaluated, yielding, respectively, 4.20×10^{-9} amp. and 3.32×10^{39} amp./cc.². Values of i_g are given in column 3 of Table 4, and the molecular polarizabilities calculated from our results, using He and SO_2 as standards, are given

in column 5. Fig. 8 is a logarithmic plot of i_g versus α_g , which is a straight line with a slope of 1.99.

With nitrogen in the cell, the estimated noise on the recorder was about 0.3 percent of the photocurrent, i.e. The drift rate amounted to 0.04*i* per hour. The estimated precision in measuring i_g for N₂ was 1 percent.

Discussion

Monodispersity of the Test Aerosols. - Before and after the experiments with the hydrosols, the Tyndall spectra was observed in the usual manner¹⁸,

(18) D. Sinclair, "Handbook on Aerosols", op. cit., Chapters 7 and 8.

after dilution to reduce secondary scattering to a negligible value. The 1 μ particles gave five red bands, the 0.5 μ particles, two, and the 0.33 μ particles, one. The spectra were at all times clear, indicating that the preparations were uniform and stable by this criterion.

Given a monodisperse hydrosol, there are several variables which must be controlled in order to produce a monodisperse aerosol by the spray-dry technique. Possible sources of heterodispersity are: (A) coagulation of particles in the aerosol state; (B) presence of dust in the solvent employed to dilute the hydrosol, or in the air streams; (C) the formation of aggregates by the evaporation of droplets containing more than one particle; (D) the formation of particles by evaporation of droplets containing only dissolved materials; (E) the deposition of dissolved substances upon a hydrosol particle by evaporation of solvent from the droplet; and (F) the formation of smaller particles by fracture of the hydrosol particles during

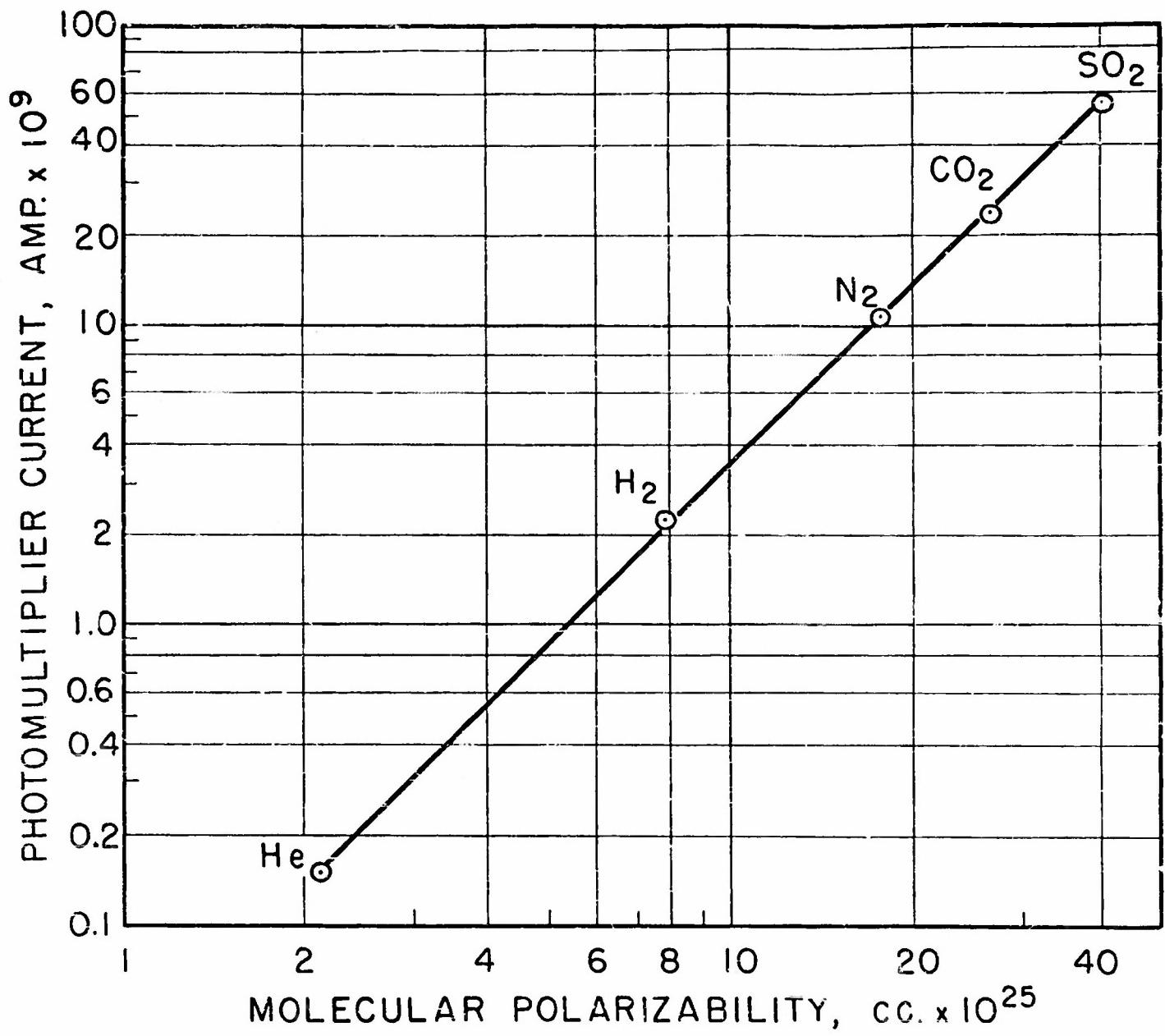


FIG. 8 LIGHT SCATTERING FROM GASES

atomization.

(A) Coagulation. The particulate concentration of the aerosol is so low under the conditions of our experiments (< 80/cc.) that the coagulation rate¹⁹ of the aerosol is several orders of magnitude less than required to

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- (19) R. Whytlaw-Gray and H. S. Patterson, "Smoke", Edward Arnold and Co., London, 1932.
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prevent difficulties from this source. Coagulation of the spray droplets, before dilution and evaporation, would be expected to be relatively more important, particularly during atomization in the air jet. However, this can be taken into account by considering the final distribution of sizes of droplets in the spray, discussed under (C) below.

(B) Contamination from Dust. Counting experiments were conducted to test possible contamination by particles in the filtered air line, and in the distilled water used to dilute the hydrosols. The filtered air count rate was negligible, typically the order of 1c./min. With diluting water, spray-dried under the experimental conditions, the count rate was also generally negligible. At the maximum sensitivity, corresponding to signals below those obtained from the 0.333μ diameter particles in Exp. 54-Zr-PS, the corrections were a maximum of 10 percent. Thus, no serious errors were introduced because of contamination by dust.

(C) The Formation of Aggregates by Evaporation. From what is known about the behavior of aerosol particles with respect to coagulation and filtration, it appears reasonable to assume that all of the hydrosol particles within a droplet will form an aggregate upon evaporation of the

droplet. The probability of aggregation will then equal the probability that the droplets will contain two or more particles. This in turn is a function of the droplet size of the spray. Such rough droplet size determinations as have been made on sprays from atomizers²⁰ lead us to expect

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- (20) T. Rosebury, "Experimental Air-Borne Infection", The Williams and Wilkins Co., Baltimore, 1947, pp. 80-82, 87-89, 131-134.
-

that the mass median diameter of droplets produced in our experiments was between one and five microns, and that only a small fraction of the number of droplets were of a diameter greater than 6μ . At a particulate concentration of the hydrosol of $10^8/\text{cc.}$, the probability that a 6μ diameter droplet will contain one particle is around 10^{-2} . The probability that a doublet will be produced by evaporation of any 6μ droplet is then 10^{-4} , or 1 percent of the number of singlets, that of triplets is 0.01 percent, etc. Thus, the formation of aggregates by evaporation of the droplets was estimated to be negligible under our usual experimental conditions.

(D) The Formation of Particles from Droplets Containing Dissolved Materials Only. The distribution of particulate masses from this source can be calculated from the weight concentration of dissolved materials in the solution and the spray droplet size distribution. Because these were not precisely known, an order-of-magnitude calculation for the largest probable droplet size (6μ) was made. Some useful relations were obtained for computations of this sort.

Let f_{λ} = volume fraction of solids in the original latex preparation,

D_{λ} = diameter of the latex particles, μ ,

n_{λ} = number of latex particles/cc. in the original preparation,

c_s = the weight concentration of dissolved non-volatile materials,

e.g., stabilizer,

n_d = the desired number of latex particles/cc. in the diluted hydrosol,

F = the dilution factor required,

D_d = diameter of a spray droplet, μ ,

w_r = weight of the residue, g., from evaporation of a spray droplet of diameter D_d ,

d_r = density of the residue,

D_r = diameter of a residual sphere formed by the stabilizer, μ .

Then

$$F = n_\lambda / n_d , \quad (2)$$

where

$$n_\lambda = 6 \times 10^{12} f_\lambda / \pi D_\lambda^3 = 1.91 \times 10^{12} f_\lambda / D_\lambda^3 , \quad (3)$$

and n_d is determined from aggregation considerations, discussed under (C) above. The weight of the residual particle can be calculated from the relation

$$w_r = 10^{-24} \pi^2 c_s n_d D_d^3 D_\lambda^3 / 36 f_\lambda , \quad (4)$$

and its diameter in microns is

$$D_r = 10^{-4} (\pi c_s n_d / 6 f_\lambda d_r)^{1/3} D_d D_\lambda . \quad (5)$$

It is readily seen from Eq. (4) that for given concentrations of dissolved material and suspended solids in the latex, and any desired aggregation probability for a given size spray droplet, the weight of the

of the residual particles to that of the latex particles is fixed by the composition of the later preparation. The relative light scattering intensity contributions will be the product of the ratio of light scattering intensities per unit of mass and the ratio of masses. A rough estimate of the scattering per unit of mass can be made from the total scattering cross section per unit of mass. This quantity is a maximum at around 0.5μ diameter.¹⁸ It decreases rapidly toward zero below this size (as D^3 in the Rayleigh region) and more slowly (as $1/D$ when $D \gg \lambda$) above this size. Thus, when the appropriately averaged residual particle diameter is much below 0.5μ , the first ratio in the product above will be small. Since the second ratio is also small, the average scattering from the residual particles was estimated to be unimportant.

The values for the relative signal per 0.47μ particle given in columns 5 and 6 of Table 2 are in agreement within the experimental accuracy of the count data. This would not be the case if the residual particles contributed significantly to the average photocurrent.

(E) The Growth of the Latex Particles by Deposition of Dissolved Materials. Employing Eq. (4), the weight of the dissolved substances in a droplet of a given diameter may be calculated. The correction to this equation required for the volume of droplet occupied by the latex particle will be small for the largest droplets, which are the only ones of possible importance. Inserting the density of the residue, d_r , the ratio of the volume of residue, v_r , obtained from evaporation of a droplet of diameter D_d , to the volume of the latex particle, v_ℓ , in a given preparation is

$$v_r/v_\ell = 10^{-12} \pi c_s n_d D_d^3 / 6 f_\ell d_r. \quad (6)$$

Considering c_s , n_d , f_λ , and d_r as constants, this quantity is seen to be independent of the size of the latex particles, and proportional to the volume of the droplet. Inserting $c_s = 0.01$, $n_d = 10^8$, $D_d = 6$, $f_\lambda = 0.3$, and $d_r = 1$, one obtains $v_r/v_\lambda = 3.8 \times 10^{-4}$. Since this ratio is small for any reasonable values of c_s , D_d , and d_r , the thickness, Δr , in microns, of the shell of residue, around the latex particle can be calculated from the relation

$$v_r/v_\lambda \approx 6\Delta r/D_\lambda. \quad (7)$$

Inserting the expression from Eq. (6) and rearranging,

$$\Delta r/D_\lambda = 10^{-12} \pi c_s n_d D_d^3 / 36 f_\lambda d_r. \quad (8)$$

With the values listed in the computation above, one obtains

$(\Delta r/D_\lambda) = 6.3 \times 10^{-5}$, for all cases of unmixed hydrosols. With mixtures of the hydrosols, this ratio will be somewhat greater. In our experiments with the 1, 0.5, and 0.3μ diameter particles, mentioned under (D), the thickness of the shell on a 0.3μ particle, formed by the evaporation of a 6μ droplet of solution around it, turns out to be less than 0.1 percent of the diameter. In this manner we concluded that size variations from source (E) were negligible in our experiments.

(F) Production of Smaller Particles by Fracture. In two experiments with the 1μ PVT, not reported here, sharp breaks were observed in the count rate curves at the expected discriminator settings, but the count rates fell off significantly from the noise level to the breaks. Observations of the Tyndall spectra gave no indication of change of the hydrosols. This led us to conclude that under certain conditions, not yet defined, some of the

particles are fractured in the atomization process. The relatively large standard deviation in experiment 11-W-PVT was also attributed to fracture. Separate experiments with 1μ diameter sulfur sols indicated virtually complete fracture. In the case of the latexes, it appears that uncontrolled variables may affect the probability of fracture in the spray-dry technique. While this is a point requiring further study, it should be noted that the position of the major break in the count rate curve agreed with that in other experiments, where difficulty was not encountered. Thus the latexes are useful as calibrating materials in spite of this effect.

Response of the Instrument as a Function of Particle Size. Because the refractive indices of polystyrene and polyvinyltoluene are essentially identical, the results of the experiments on the two may be compared directly.

The results for the mean values of the (peak) photocurrents obtained from the various counting experiments, and normalized as described above, are summarized in Table 5.

Table 5. Comparison of Signals from the Different Particles

Experiment	Particle Diameter D_p, μ	Normalized		
		Mean Peak Photocurrents, (amp. $\times 10^9$)	$\frac{D^2}{\lambda}$	$\left(\frac{\text{Photocurrent}}{D^2 \lambda}\right) \times 10^9$
Oscillographic	0.936	6.7	0.97	$6.9 \pm .5$
11-W-PVT	0.986	7.9	0.97	$8.2 \pm .6$
12-Zr-PVT	0.986	8.4	0.97	$8.7 \pm .6$
53-Zr-PS	0.514	2.36	0.264	$8.9 \pm .6$
Oscillographic	0.470	1.50	0.220	$6.8 \pm .5$
54-Zr-PS	0.333	1.09	0.111	$9.8 \pm .7$

Column 5 contains values of the peak photocurrents divided by the diameter in microns, squared. The uncertainties indicated in the same column represent our estimates of the probable precision. These were based upon an evaluation of errors due to variations in light source intensity, amplifier gain, discriminator bias voltage drift, and photomultiplier gain. Errors introduced during the photometric measurements on air, which were required for normalization, were relatively small.

The figures in column 5 may be interpreted as a quantity proportional to the scattering coefficient K, which we define as the ratio of the effective scattering area per particle to the geometric area. K is a function of the particular optical system, and should not be identified with the scattering coefficient, employed by Sinclair¹⁸ and others. The results of the

oscillographic experiments should not be compared directly with the others, because of changes in the slit dimensions between the two groups of experiments. K is constant within the experimental precision, for results obtained with the Zr source. Within themselves, the results of the oscillographic experiments also indicate that K is constant.

It is of particular interest that the experiment, 11-W-PVT, with the tungsten source, yields a value of K practically the same as the average value for the concentrated arc source. This indicates that the normalization procedure developed here, and based upon air as a scattering standard, makes the results with the two sources comparable. This is attributed to similarity of the spectral emission curves from the two sources. The spectral region of interest is between 3750 and 5750 Å²¹, determined primarily by the

(21) C. T. O'Konski, M.S. Thesis, Northwestern University, June, 1946.

spectral response of the photomultiplier and the spectral energy distribution from the source. Examination of the emission curves for the tungsten source²², and the concentrated-arc source,²³ reveals that the curves can be

(22). H. J. Reich, "Theory and Applications of Electron Tubes", McGraw-Hill Book Co., Inc., New York, 1944, p. 539.

(23) W. D. Buckingham and C. R. Deibert, J. Soc. Motion Picture Eng. 47, 376 (1946).

superposed in this region, after appropriate normalization.

It can not be concluded from the results on particles of 0.3, 0.5 and 1μ diameter that the value of K will be the same for larger particles. In fact, there is some question as to the applicability of a constant value between the points. It is quite probable that further and more accurate work with a more complete spectrum of sizes will show some dependence of K upon diameter within this region.

Eventually, when more complete tables of values for the light scattering functions become available, it will be possible to calculate the response of the counter to spherical particles. Such computations will involve numerical integrations over the spectral response region and the solid angles of the illuminating and viewing systems, and are at best extremely laborious. It appears that the more expeditious procedure at the present time is to standardize the optical system, and establish the response curve by experiment.

Sensitivity of the Counter to Small Particles. A current is set up in the photomultiplier by the background light flux, which is produced by scattering of the incident light by the gas within the total scattering volume, and by stray reflections and diffraction effects. In all the optical systems we have tested (references 3, 5, and this research) the background photocurrent is at least an order of magnitude greater than the dark current of a good photomultiplier. The shot fluctuations in this photocurrent produce a random background signal, referred to as noise. The noise is superposed upon the signals from particles, and it sets a limit on the smallest signal which can be detected. With the final optical system, used in

experiments 53 and 54-Zr-PS, the signal-to-noise ratio was 3.3 for the 0.333μ diameter particles. Because of the rapid decrease of noise count rate with increasing discriminator voltage, which can be seen from Fig. 7, setting the discriminator to a voltage 50 percent above the 300 c./min. noise level reduced the count rate to about one per minute. At this voltage, over 98 percent of the particles were counted.

With the tungsten source, the lower limit of size which can be counted is 0.3μ diameter. This figure was estimated from the results in Table 3, and corresponds to practically complete counting of particles, with the noise contributing about 1 c./min. The lower limit with the Zr source will be very near 0.25μ diameter. This estimate was based in part upon some unpublished approximate light scattering computations by the group at Indiana University* for the right-angle optical system. The tungsten source

* Private communication from F. T. Gucker, Jr.

is preferred for most applications because of its greater stability. Data on source intensity fluctuations is quoted under Resolving Power of the Counter below. Such fluctuations could be tolerated only because of the extremely low stray light in our right-angle optical system. In cases where sensitivity and resolving power in the 0.3μ region is of paramount importance, the concentrated arc sources are to be preferred. The 300 watt unit could be used at an image-to-object ratio of unity, with some improvement in sensitivity over the 100 watt source.

The sensitivity to small signals can be approximately doubled by employing helium gas to dilute the aerosol. From the results given in Tables 3 and 4, it can be shown that this will reduce the background flux by a factor of 3.3, and decrease the noise level by a factor of 1.8. Additional improvement could be obtained with more intense light sources, further decreases in the stray light and optical and flow system modifications which will make possible the use of response systems of narrower band

width. Improvements of 100-fold in such factors would increase the signal-to-noise ratio by approximately 10, and decrease the diameter of the smallest particle which can be detected by a factor which we estimate will be between 1.5 and 2.5. The factor in particle diameter is small relative to the improvement in signal-to-noise ratio, because of the rapid decrease of signal per particle below around 0.3μ diameter.

Resolving Power of the Counter. Employing the observed dependence of the signal upon the particle diameter, the measured standard deviations in the diameter were computed for the experiments with the concentrated arc source. These are listed in Table 6.

Table 6. Standard Deviations in the Particle Diameter

<u>Diameter of Particle, μ</u>	<u>Standard Deviation, μ</u>
0.986	0.080
0.514	0.036
0.333	0.018

The standard deviations may be regarded as a measure of the resolving power, or resolution, of the particle counter. Equal peaks in a bimodal distribution, consisting of two sizes only, should be clearly visible if the separation between the peaks is 3 times the standard deviation. With uniform particles, the uncertainty in determining the mean diameter will be less than the standard deviation, by a factor depending somewhat upon the number of particles characterized.

If the pulses obtained from all of the particles of a given size were exactly equal in emplitude, then one might expect to make the resolving

power as high as desired by refining the electronic discriminator circuits to the desired degree. Our results indicate, however, that the attainable resolving power is determined by other factors, which may include (A) variations in pulse length, coupled with limitations of the frequency response of the amplifier, (B) superposition of random noise upon the signals, (C) variations in illumination of the particles, (D) variations of the aperture of the light collecting system, and (E) count rate errors. These will be considered in sequence.

(A) Pulse Length Variations and Frequency Response Limitations. If the scattering signals were of equal peak amplitudes, but non-equal durations, the amplitudes of the electrical signals would be spread into a distribution which would be a function of the distribution of pulse durations and the frequency response of the electrical system. The overall frequency response was determined primarily by the time constant of the photomultiplier output circuit, which was 0.2 msec. For 1 msec. pulses the resulting spreading was estimated to be around \pm 5 percent for durations varying by \pm 50 percent, and < 1 percent for a variation of \pm 10 percent.

Pulse durations were measured in the oscillographic experiments. The average deviation of the mean was 10 percent, which was the estimated precision of the measurements. This indicates that the flow system possesses the desired characteristic that all particles are illuminated for periods which are equal within the precision of the measurements. Thus, the effects upon resolving power arising from variations in pulse length were relatively unimportant in this work.

(B) Effect of Random Noise. With signals of exactly equal amplitudes, there will be a spreading of the measured pulse amplitude distribution produced by the random noise. The noise level which is pertinent here is that corresponding to the flux prevailing when the particle is within the sensitive volume. The noise is proportional to the square root of the background flux²⁴. For very small particles, at the threshold of sensitivity,

(24) See, e.g., R. W. Engstrom, J. Opt. Soc. Am., 37, 420 (1947).

the increase of noise produced by scattering from the particle was negligible. For large particles which produce a photocurrent which is much greater than the background flux, the noise level increases approximately as the square root of the signal. Then the signal-to-noise ratio will be proportional to the square root of the signal, or to the diameter of the particle. From these considerations, we conclude that the percent spread of the pulse amplitudes produced by noise should vary inversely as the first power of the diameter for large particles ($> 0.5\mu$), and more rapidly for smaller ones. In our experiments, the average deviation of the pulse amplitudes from the mean was a measure of the spreading from all causes. Since the values with the concentrated arc source given in Table 3 are essentially constant for 1μ , 0.5μ , and 0.3μ diameter particles, the deviations can not be attributed to the effect of random noise.

The spread of signal amplitudes caused by noise can be computed approximately from count rate curves of the type shown in Fig. 7. Some calculations based upon these curves showed that the magnitude of the standard deviation attributable to noise alone was well under the value

observed experimentally, even for the 0.333μ diameter particles. This supports the conclusion that other factors are responsible for the greatest portion of the observed standard deviation.

(C) Variations in Illumination. Here one must consider the stability of the light source, and the uniformity of illumination over the sensitive volume. The tungsten source, operated from a battery and charger, was stable within around 1 percent during the counting experiments. The concentrated arc sources were stable to within 1 or 2 percent in certain experiments. In others, variations of 10 percent were sometimes observed. The maximum standard deviation in any one experiment was 5 percent. We conclude that instability of the concentrated arc source contributed significantly, but did not account for all of the standard deviation.

The optical and flow systems were those especially designed^{3,5} to ensure that all particles would cross a zone within the sensitive volume in which the intensity of illumination reaches the same peak value. A precise experimental study would be required to evaluate the effect of the non-uniformity of illumination upon the resolving power.

(D) Non-uniformity of Aperture of the Collecting System. Some variation in signals from identical particles, uniformly illuminated, may be expected because different particles follow different flow lines within the aerosol stream. With the optical design and the flow system employed here, the sensitive volume is small and is precisely defined in all dimensions by the slits and the boundary between the aerosol stream and the flowing air sheath. Since the possible range of positions of aerosol particles within the sensitive volume is small compared to the focal

length of the collecting lenses, the contribution to the standard deviation from non-uniformity of aperture is expected to be small, possibly a few percent.

(E) Count Rate Errors. When count rates are measured with a single channel scaler, errors are introduced by variations of the aerosol concentration and the sampling rate during the period of a complete experiment, which is generally around 1 hour. This is illustrated by the scatter of the points of Fig. 5 between one and 10 volts. These points were obtained at intervals during the course of the experiment to establish the magnitude of the fluctuations, which average less than 4 percent. Along the steep portion of the curve, the variations are comparable but less obvious. Portions of the standard deviations in experiments 11 and 12 can be attributed to these variations. In experiments 53 and 54, with the two channels, the procedure which we followed automatically compensated for the concentration and sampling rate fluctuations, so errors from these sources were eliminated.

It appears that the only advantage to be gained from a multiple channel counting system is that the entire distribution curve could be obtained more quickly. The use of differential channels, which can easily be incorporated into the type of system described here by use of anticoincidence circuits, would result in a direct presentation of the differential distribution curve.

Sensitivity and Stability of the Photometer. The precision of the normalized mean pulse currents depends partly upon the uncertainties in the measurements of the photocurrent due to light scattering from air. The air scattering was obtained from the difference between the total photocurrents with air and with helium in the total scattering volume of the cell. No corrections were applied for the barometric pressure and room temperature variations. These together could introduce an uncertainty of the order of 2 percent. The error estimated from all causes, for those experiments employing the tungsten source, was 3-4 percent. Larger estimates of 7 percent for 53-Zr-PS and 5 percent for 54-Zr-PS reflect the additional contribution of intensity fluctuations of the Zr source.

Photometric measurements of the light scattering intensity from the 0.470μ aerosol relative to the scattering from the 0.986μ aerosol, given in column 6 of Table 2, have a probable error of 16 percent. One contribution there was the fluctuation in the number of particles passing through the sensitive volume during times comparable with the integrating time constant of the photometer, which was about 0.5 second. This variation would have been reduced by increasing the time constant. Another arose from variations in aerosol concentration.

The probable error of the measurements of the total flux with gases in the cell, listed in column 2 of Table 4, were at most 2 percent. The disagreement between columns 4 and 5 is significantly larger than this figure for two cases, H_2 and CO_2 . For H_2 the disagreement probably arises because the gas scattering photocurrent is a small fraction of the total. In the case of CO_2 , depolarization corrections, not applied, and impurities

may be contributing factors. In Fig. 8, the straight line with slope 1.99, is in excellent agreement with uncorrected Rayleigh theory, which predicts 2.00.

It is convenient, for comparison with previous photometers², to state the sensitivity in terms of a 0.3μ diameter aerosol with a refractive index around 1.5. It can be shown from the data of Tables 2, 3, and 4 that such an aerosol having a particulate concentration of 210 cc.^{-1} , or a mass concentration of $3.3 \times 10^{-9} \text{ g./liter}$, will give a scattering photocurrent equal to that from the air. With the tungsten source, the smallest detectable concentration would be around 1 percent of this or $4.0 \times 10^{-11} \text{ g./liter}$. With aerosol in the sensitive volume only the corresponding mass concentration would be $9.0 \times 10^{-11} \text{ g./liter}$.

For photometric measurements, the advantage of the larger scattering photocurrents obtained with the Zr source is offset by the greater instability, which makes it less suitable than the tungsten source.